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I. L. Fine

Use of Barium Salts in Water Softening

USE OF BARIUM SALTS IN WATER SOFTENING

BY

ISADORE LEONARD FINE

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCE

UNIVERSITY OF ILLINOIS

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..... June 5 1920

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

..... Isadore Leonard Fine

ENTITLED..... Use of Barium Salts in Water Softening

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF..... Bachelor of Science

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..... Edward Bartow

Instructor in Charge

APPROVED:..... W. A. Koyne

HEAD OF DEPARTMENT OF..... Chemistry

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USE OF BARIUM SALTS IN WATER SOFTENING

Vast amounts of money are expended annually by the various industrial concerns in the conversion of water into steam either for heating purposes or for the development of motive power. As a result of this conversion the impurities in the water are concentrated or precipitated as a sludge or scale.

The most common of these impurities are:

Carbonates of calcium, magnesium, sodium and potassium

Sulphates " " " " " "

Nitrates " " " " " "

Chlorides " " " " " "

SiO_2 , Fe_2O_3 and Al_2O_3

Suspended matter

Carbonic acid

The carbonates of lime and magnesium form a soft scale or sludge and unless mixed with the sulphates of calcium and magnesium can be "blown off" or easily removed.

Sulphates of calcium and magnesium produce a hard scale which interferes with the conductance of heat to the water thereby causing a loss in efficiency. The difference in the coefficient of expansion between the scale and the boiler plates causes the scale to crack and the entrance of water into these cracks give very favorable chances for excessive heating of the boiler plate and explosions.

SiO_2 is very seldom present in large quantities; therefore, but little is present in the scale. SiO_2 is easily precipitated by boiling the water but if heated for long periods it forms a hard scale.

Nitrates and chlorides of calcium and magnesium cause a hard scale to form when present in water containing carbonates. Nitrates and chlorides of calcium and magnesium upon hydrolysis form free HCl and HNO₃ which are very corrosive. Carbonic acid also causes corrosion of the boiler plates.

Salts of sodium and potassium often present a serious problem as they tend to cause foaming. This tendency is greatly increased by the presence of finely divided matter in suspension. When foaming takes place water is carried as steam bubbles into the pipes and engine and often does great damage.

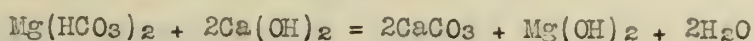
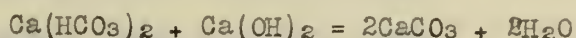
Water is generally softened either by distillation, heating, chemical precipitation or by the use of compounds which have the property of exchanging their bases for the bases in the hardening constituents of the water.

Distillation although an ideal method is too expensive to be used very extensively.

In heating water to be softened, the carbon dioxide is driven off and the carbonates of calcium and magnesium are precipitated. This method only rids the water of its temporary hardness.

The base exchanging substances usually contain alkali metals, aluminium and silica in molecular combination. The alkali metals are easily interchangeable with each other and with other bases and may be regenerated by treatment with the appropriate salt solutions.¹

Precipitation by the addition of chemicals is the most widely used. Clark in 1841 patented his softening process which consisted of the addition of lime to remove the carbonic acid and also the carbonates of calcium and magnesium.⁴



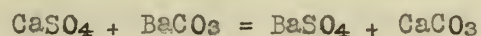
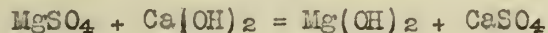
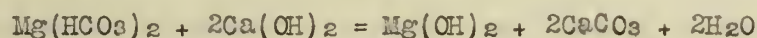
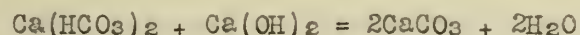
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Dr. Porter followed with his method in which he used soda-ash to remove the sulphates of calcium and magnesium by precipitating them as the calcium and magnesium carbonates.

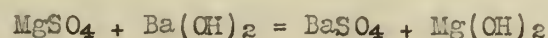
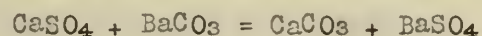
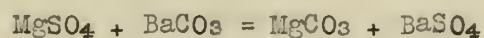
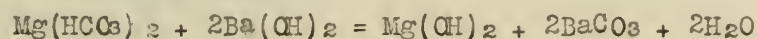
In 1886 Wm McNab and G.L.Beckett discovered that caustic soda or lime and soda-ash were necessary for the complete removal of the magnesium.⁶

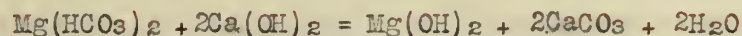
The lime barium method for softening water removes the temporary hardness by means of lime as in the Clark process while the BaCO_3 , whose solubility is 24 milligrams per liter of water, precipitates any sulphates present as the insoluble BaSO_4 whose solubility is only 2.3 milligrams per liter of water.³



Because only 24 milligrams of BaCO_3 are soluble per liter of water an excess of this reagent would not be detrimental to the boiler when added to the water in large quantities.

Barium hydroxide removes the sulphates of calcium and magnesium and the calcium and magnesium hydroxides thus formed precipitate the bicarbonates. These reactions may be considered in the reverse order, that is, that the $\text{Ba}(\text{OH})_2$ first reacts with the bicarbonates and the BaCO_3 thus formed precipitates the sulphates.⁵





EXPERIMENTAL

Because the lack of information concerning the practical value of barium carbonate, barium hydroxide compared with lime and lime and soda, a number of experiments were made to show their relative value. For each treatment six samples of one and one-half liters each were treated with varying amounts of the reagents. The lime, soda-ash and barium hydroxide were added as solutions while barium carbonate because of its great insolubility in water was added as a solid. The samples to which BaCO_3 were added were put upon a shaking machine and shaken for two hours. After treatment the samples were allowed to stand for several days with frequent shakings.

The following tests were made of the water before treatment.

1. Non-carbonate hardness
2. Magnesium
3. Sulphates
4. Nitrates
5. Chlorides
6. Alkalinity
7. Total Residue

The Methods of Analysis

1. Determination of non-carbonate hardness.

Place 200 cc. of the sample into a 500 cc. Erlenmeyer flask and boil for

fifteen minutes to expel the CO_2 . Then add 25 cc. of soda reagent (equal volumes of N/10 NaOH and N/10 Na_2CO_3), boil ten minutes and filter into a 200 cc. volumetric flask. In an aliquot portion the excess of alkali is titrated with N/50 H_2SO_4 using methyl-orange as an indicator. A blank determination is also made using distilled water. The difference between the number of cc. used for the blank and the number of cc. used for the sample is the non-carbonate hardness in terms of CaCO_3 .

2. Determination of Magnesium.

Place 200 cc. of the sample into an Erlenmeyer flask and neutralize accurately with N/50 H_2SO_4 using methyl orange as indicator. Boil for ten minutes to expel the CO_2 and then add 50 cc. of a saturated solution of lime water, boil for a minute and allow to cool. Transfer to a 200 cc. volumetric flask and dilute to the mark with CO_2 free distilled water. Filter and titrate excess of lime water in an aliquot portion with N/50 H_2SO_4 using methyl orange as indicator. Make a blank determination using distilled water. The difference between the number of cc. used for the sample and the number of cc. used for the blank is the amount of magnesium present in terms of CaCO_3 .

3. Determination of sulphates.

Evaporate 200 cc. of the sample to 100 cc., make acid with hydrochloric acid, and add a slight excess of barium chloride to the hot solution. Allow to stand on the hot plate until the precipitate settles readily. Filter off the precipitate, wash, ignite and weigh as barium sulphate.

4. Determination of Nitrates.

Add 2 cc. of a 33% nitrogen free sodium hydroxide solution to 100 cc. of the sample in a casserole and concentrate rapidly to a volume of 20 cc. to remove the ammonia nitrogen. Rinse into a test tube and dilute to 70 cc. with

nitrogen free water. Insert a piece of aluminium .4 inches long weighing .5 grams into the tube. Close with a stopper through which passes a tube leading to a second test tube containing water, allow to stand over night when the reduction of the nitrates to ammonia is completed. Rinse the solution together with the strip of aluminium into a Kjehldahl flask and distill 200 cc. into a volumetric flask. Determine the ammonia in an aliquot portion by nesslerization.

5. Determination of Chlorides.

Titrate 50 cc. of the sample with standard silver nitrate solution using potassium chromate as indicator.

6. Determination of Alkalinity.

Place 50 cc. of the sample into a 200 cc. Erlenmeyer flask, add a drop of phenolphthalein as indicator. If solution remains colorless the hydroxides and normal carbonates are absent. If colored add n/50 sulfuric acid until the color just disappears. Add three or four drops of methyl orange indicator and continue the titration until the yellow color begins changing to orange red.

7. Determination of Total Residue.

Evaporate 100 cc. of the sample on the steam bath in a weighed dish. Dry for an hour at 180° Centigrade, place in dessicator and when cool weigh again.

The following tests were made upon the treated water.

1. Calcium
2. Magnesium
3. Alkalinity
4. Sulphates
5. Chlorides
6. Total Residue

1. Determination of Calcium.

Evaporate 250 cc. of the sample to 100 cc. and make alkaline with ammonium hydroxide. Add little by little an excess of ammonium oxalate to the hot ammoniacal solution. Keep warm and stir at intervals until the precipitate settles readily. Filter, wash, ignite and weigh as calcium oxide.

2. Determination of Magnesium.

Acidify filtrate from calcium determination with hydrochloric acid and concentrate to 100 cc. Add 20 cc. of a saturated solution of microcosmic salt, cool and make distinctly alkaline with ammonium hydroxide. Allow to stand over night, filter, wash with 3% ammonium hydroxide, ignite and weigh as magnesium pyrophosphate.

3. Determinations of alkalinity, sulphates, chlorides and total residue are made as previously described.

Cunningham Home

Determinations made Pts. per million	Reacting value	Combining value
Residue	598	
Nitrate	1.36 x 0.0161 =	.022
Chlorine	12 x 0.0282 =	.3384
Sulphate	122.1 x 0.0208 =	2.5397
Alk. as CaCO ₃	390 x 0.02 =	<u>7.80</u>
		10.6803

Non-carbonate hardness 128

Magnesium as CaCO₃ 202 x .02 = 4.04

Calcium as CaCO₃ 316 x .02 = 6.32

10.36

10.6803 - 10.3600 = .3203 Combining value of Sodium & Potassium

Salt	Mg. Equivalents per liter		Equivalent wt. of salt	p.p.m.
NaNO ₃	.022	x	85.01	1.87
NaCl	.2983	x	58.46	17.44
MgCl ₂	.0401	x	47.52	1.90
MgSO ₄	2.5397	x	60.19	152.87
MgCO ₃	3.6615	x	42.16	61.56
CaCO ₃	6.32	x	50.03	<u>316.19</u>
				551.83

Cunningham Home

Lime-Treatment

p.p.m.

Ca(OH) ₂ added as CaCO ₃	Total Resi- due	Alk. to Ph.	Alk. to M.O.	Calcium	Magnesium	Sul- phate	Chloride
0	598	0	390	125.2	49.3	122.1	12
459	328	20	62	58.1	41.6	122.1	12
530	291	22	44	42.3	30.5	122.1	12
595	282	26	30	24.6	20.7	122.1	12
671	292	36	46	38.8	10.6	122.1	12
742	333	66	82	62.4	5.7	122.1	12

Lime-soda Treatment

p.p.m.

Ca(OH) ₂ added as CaCO ₃	Na ₂ CO ₃	Total Resi- due	Alk. to Ph.	Alk. to M.O.	Calci- um	Magnes- ium	Sul- phates	Chlorides
0	0	598	0	390	125.2	49.3	122.1	12
459	53	294	30	86	32.6	42.1	122.1	12
530	106	286	38	60	16.8	33.2	122.1	12
595	159	276	44	78	9.5	23.6	122.1	12
671	212	292	48	74	4.2	11.4	122.1	12
742	265	326	78	102	3.7	6.2	122.1	12

Line- BaCO₃ Treatment

p.p.m.

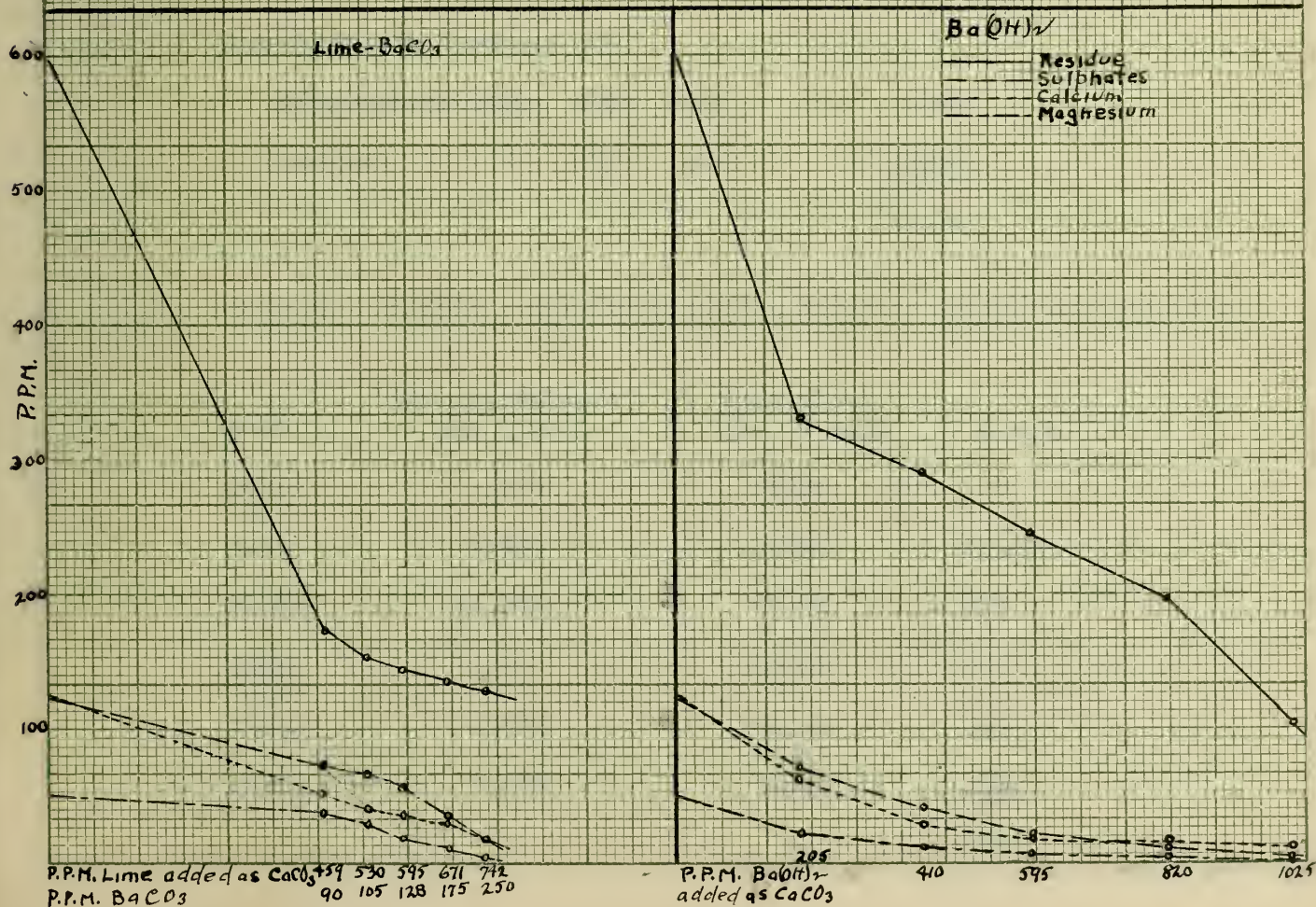
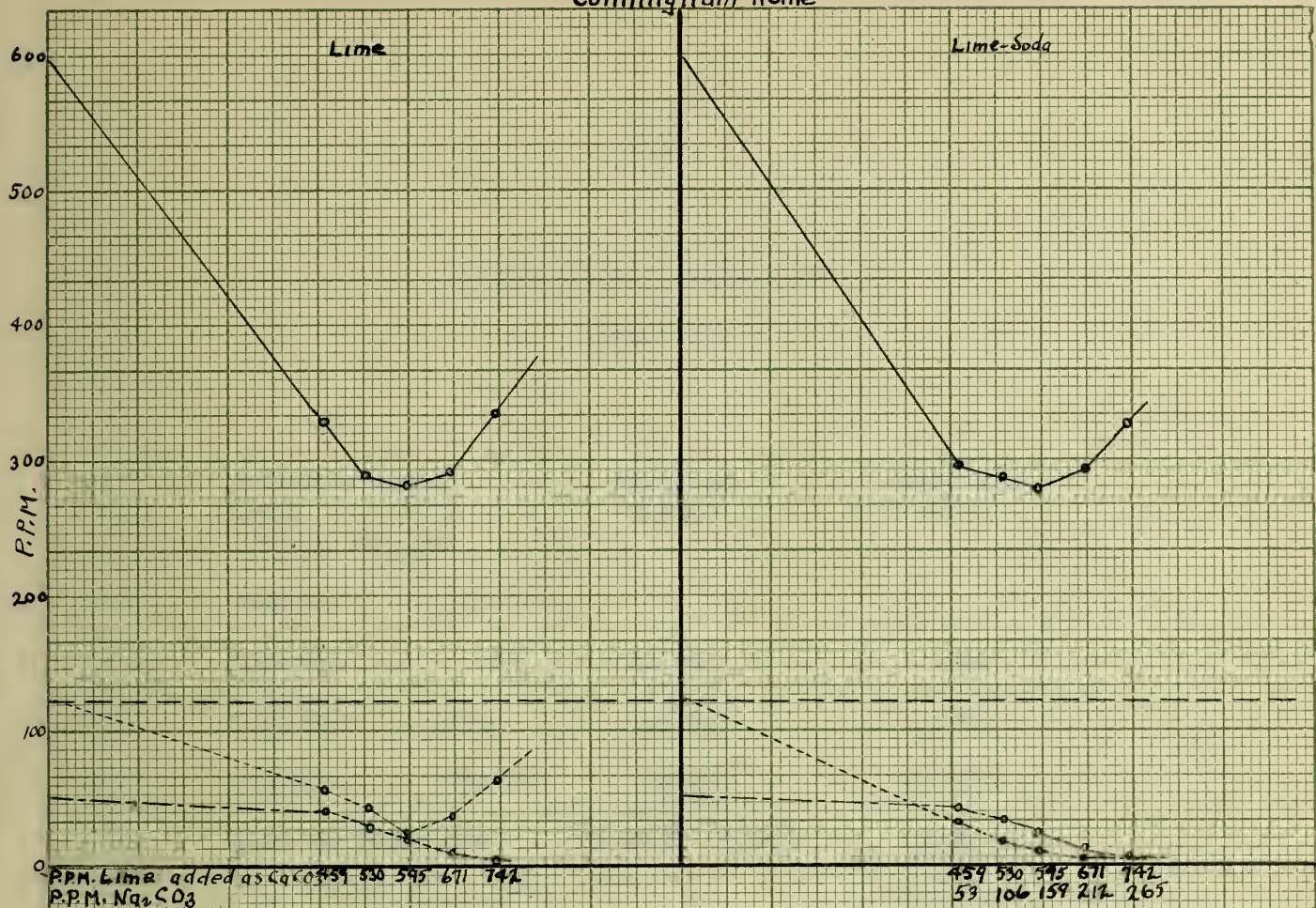
Ca(OH) ₂ added as CaCO ₃	BaCO ₃	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	0	598	0	390	125.2	49.3	122.1	12
459	90	175	16	78	47.6	38.4	75.9	12
530	105	154	18	60	41.6	27.6	68.8	12
595	128	145	22	54	36.4	18.7	58.1	12
671	175	136	24	42	29.7	10.1	37.5	12
742	250	127	28	33	17.3	4.8	16.7	12

Ba(OH)₂ Treatment

p.p.m.

Ba(OH) ₂ added as CaCO ₃	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	598	0	390	125.2	49.3	122.1	12
205	331	88	208	60.3	20.7	71.5	12
410	288	112	170	28.9	11.9	42.2	12
595	244	114	96	16.6	6.7	20.1	12
820	197	132	74	12.9	3.1	8.7	12
1025	103	154	52	9.6	.5	4.6	12

Cunningham Home



Hypothetical Combinations

Roseville

Determinations made Pts per million		Reacting value	Combining value
Residue	2085		
Nitrate	.87	0.0161	.014
Chlorine	174	0.0282	4.907
Sulphate	986.2	0.0208	20.5129
Alk. as CaCO_3	252	0.02	<u>5.04</u>
			30.4739

Non-carbonate hardness 366

Magnesium as CaCO_3	220	0.02	4.40
Calcium " "	398	0.02	<u>7.96</u>
			12.36

$30.4739 - 12.3600 = 18.1139$ combining value of sodium and potassium

Salt	Mg. Equivalents per liter	Equivalent wt. of salt	p.p.m.
NaNO_3	.014	85.01	1.2
NaCl	4.907	58.46	286.8
Na_2SO_4	13.232	71.03	939
MgSO_4	4.40	60.19	264
CaSO_4	2.876	68.06	195
CaCO_3	5.048	50.03	<u>253</u>
			1940

Roseville

Lime-Treatment

p.p.m.

Lime added as CaCO_3	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	2085	0	252	159.2	53.3	986.2	174
328.3	1504	12	52	143.7	38.4	986.2	174
394	1293	16	46	108.4	25.4	986.2	174
472.8	1191	22	42	83.8	18.3	986.2	174
525	1326	26	48	143.2	10.6	986.2	174
591	1675	34	56	229.3	6.2	986.2	174

Lime-Soda Treatment

p.p.m.

Ca(OH)_2 added as CaCO_3	Na_2CO_3	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlori- des
0	0	2085	0	252	159.2	53.3	986.2	174
328.3	424	1362	0	46	48	38.1	986.2	174
394	493	1248	0	40	34	25.9	986.2	174
472.8	530	975	0	36	28	18.8	986.2	174
525	636	1144	0	32	22	10.2	986.2	174
591	742	1529	0	28	14	6.1	986.2	174

Lime-BaCO₃ Treatment

p.p.m.

Ca(OH) ₂ added as CaCO ₃	BaCO ₃	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	0	2085	0	252	159.2	53.3	986.2	174
328.3	450	1027	36	114	25.6	35.6	666.8	174
394	550	926	42	78	17.5	23.8	600.4	174
472.8	650	708	60	122	11.8	14.9	532.2	174
525	750	795	70	130	7.2	8.2	474.6	174
591	850	906	78	144	3.8	5.6	424.3	174

Ba(OH)₂ Treatment

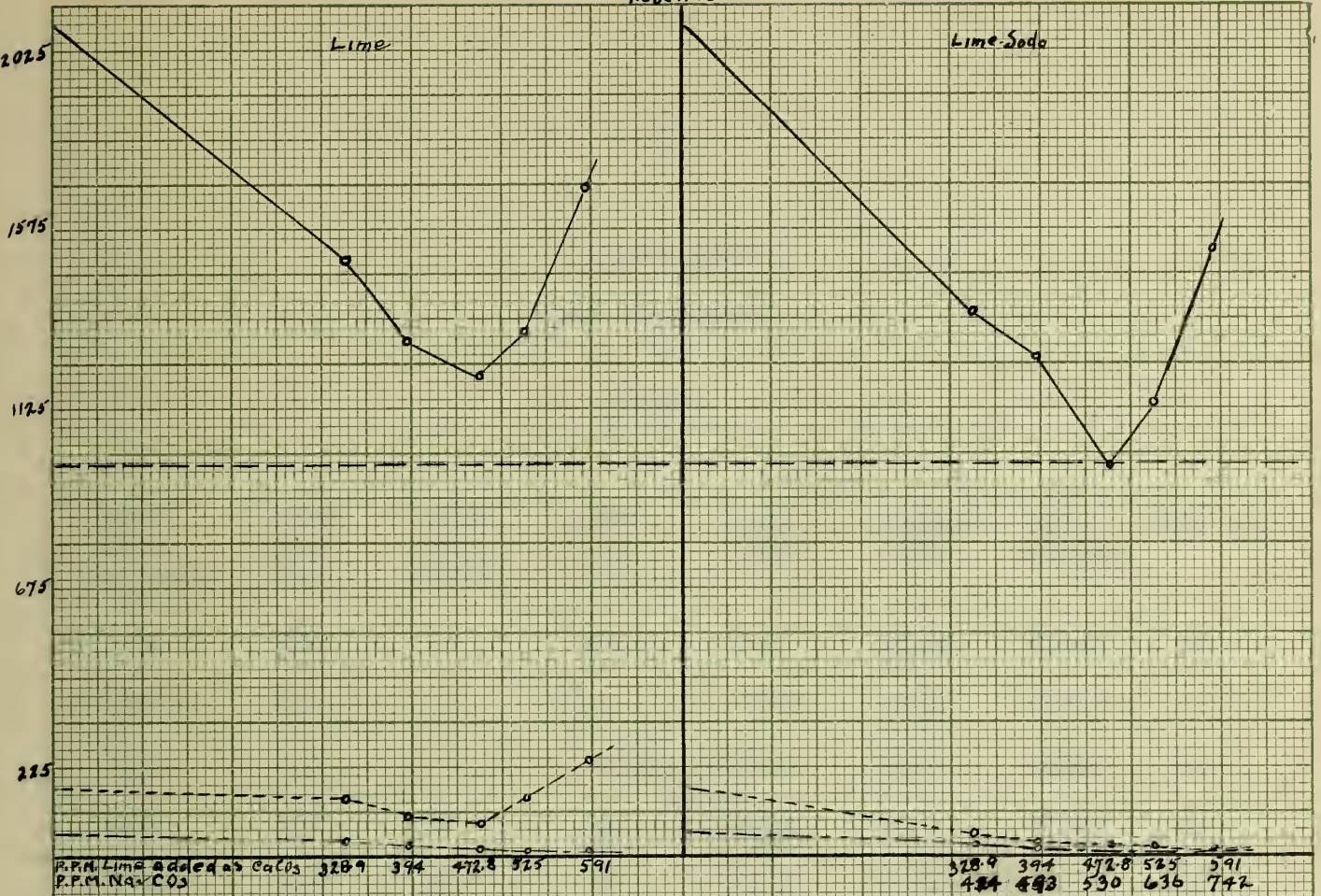
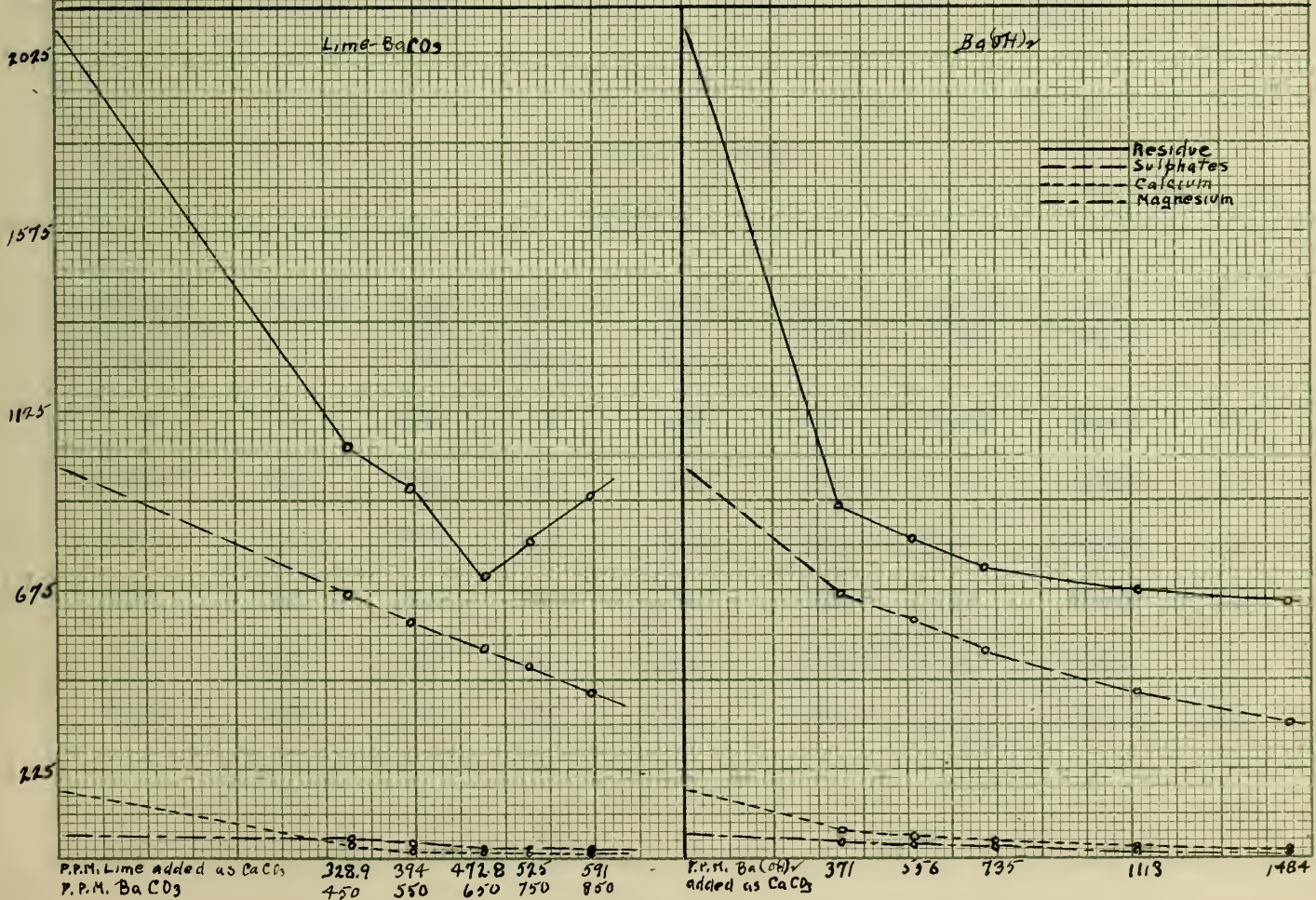
p.p.m.

Ba(OH) ₂ added as CaCO ₃	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	2085	0	252	159.2	53.3	986.2	174
371	880	16	212	59.9	40.2	660.5	174
556	792	36	182	49.7	26.4	596.4	174
735	724	50	138	30.2	15.8	511.1	174
1113	669	62	106	18.4	4.1	414.3	174
1484	627	70	92	8.8	0	331.2	174

Roseville

Lime

Lime Soda

Lime- BaCO_3 Ba(OH)_2 

Bloomington

Lime- Treatment

p.p.m.

Lime added as CaCO_3	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	936	0	426	216	55.45	310.9	15
393.8	805	0	100	176.8	47.4	310.9	15
525	707	8	48	138.9	40.9	310.9	15
656	685	18	40	107.5	36.4	310.9	15
787.5	734	26	46	128.6	25.8	310.9	15
918.8	815	38	56	164.5	18.4	310.9	15

Lime-Soda Treatment

p.p.m.

Ca(OH)_2 Added as CaCO_3	Na_2CO_3	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlori- des
0	0	936	0	426	216	55.45	310.9	15
393.8	250	769	16	152	56.5	47.3	310.9	15
525	300	682	46	146	49.7	40.7	310.9	15
656	348	546	60	140	35.7	36.2	310.9	15
787.5	400	627	64	136	43.6	25.7	310.9	15
918.8	500	785	76	130	50.4	18.2	310.9	15

Hypothetical Combinations

Bloomington

Determinations made Pts. per million		Reacting value	Combining value
Residue	936		
Nitrate	1.64	0.0161	.0264
Chlorine	15	0.0282	.4230
Sulphate	310.9	1.0208	6.4667
Alk. as CaCO ₃	426	0.02	<u>8.52</u>
			15.4361

Non-carbonate hardness 342

Magnesium as CaCO ₃	228	0.02	4.56
Calcium " "	540	0.02	<u>10.80</u>
			15.36

15.4361 - 1536 = .0761 combining value of sodium and potassium

Salt	Mg. Equivalents per liter		Equivalent Wt. of salt		p.p.m.
NaNO ₃	.0264	x	85.01	=	2.24
NaCl	.0497	x	58.46	=	2.90
MgCl ₂	.3733	x	47.62	=	17.77
MgSO ₄	4.1867	x	60.19	=	251.99
CaSO ₄	2.24	x	68.06	=	152.45
CaCO ₃	8.56	x	50.03	=	<u>428.25</u>
					855.6

Lime - BaCO₃ Treatment

p.p.m.

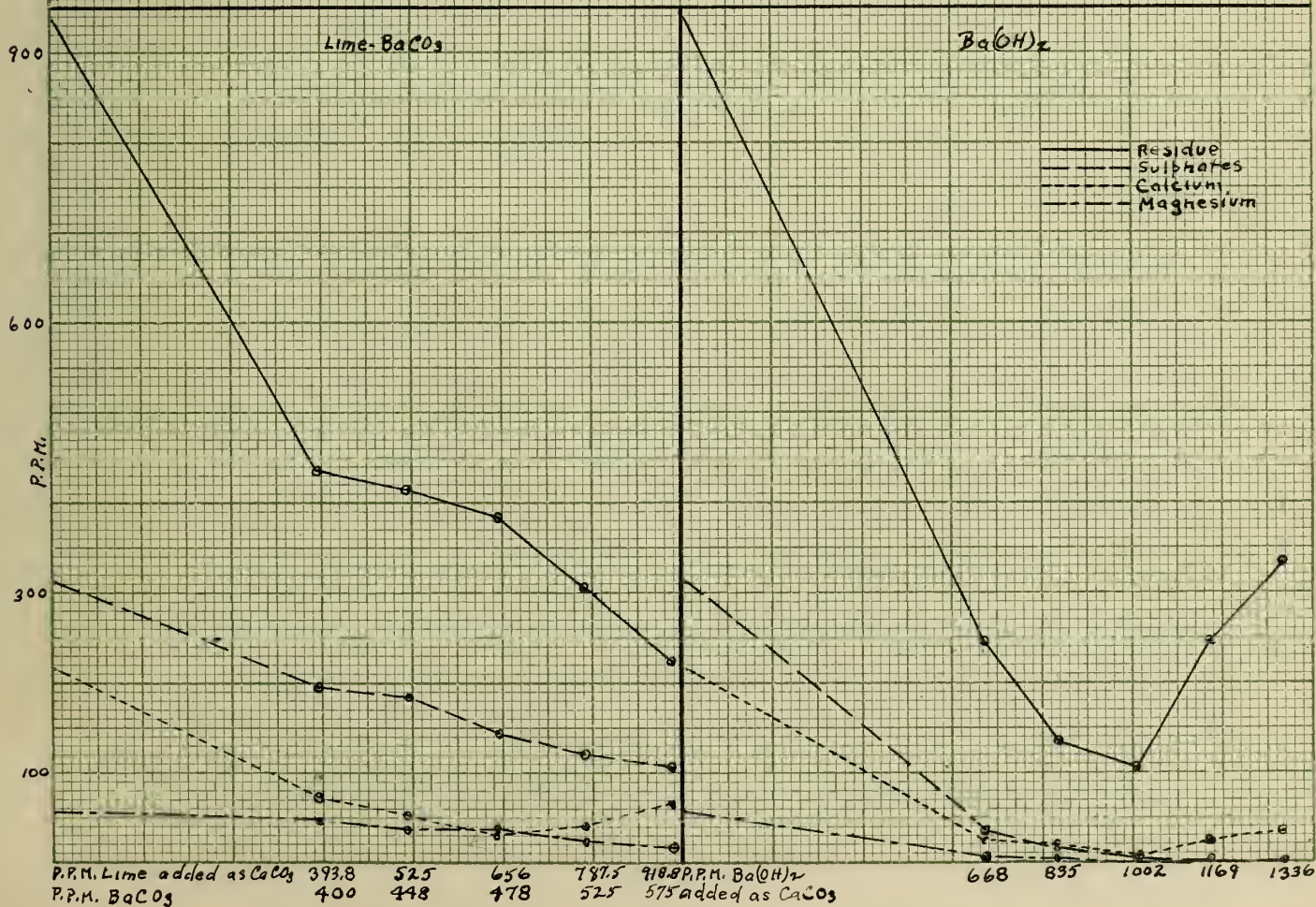
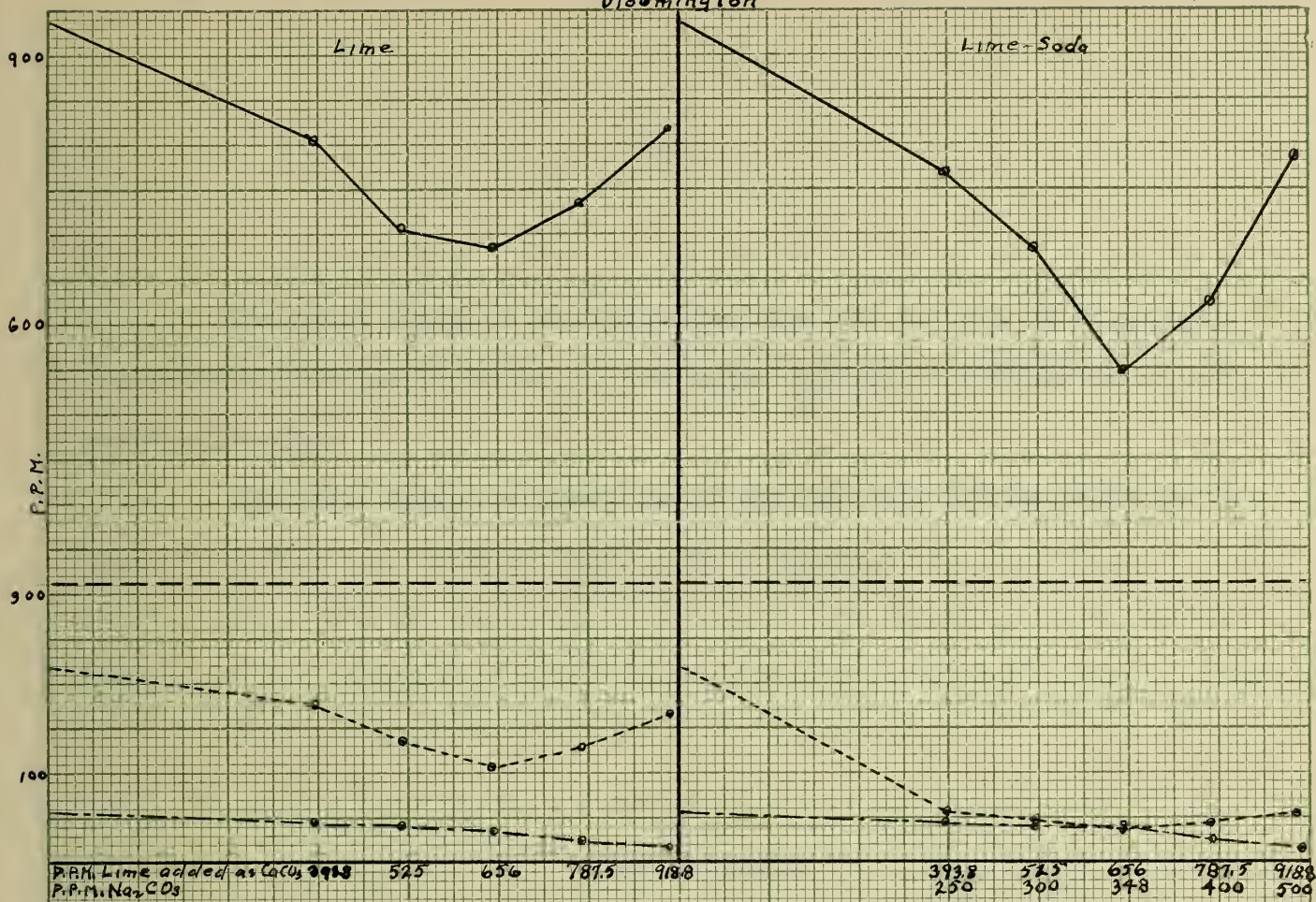
Lime added as CaCO ₃	BaCO ₃	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlorides
0	0	936	0	426	216	55.45	310.9	15
393.8	400	437	4	165	72	46.5	196.8	15
525	448	412	16	117	50.4	39.9	185.5	15
656	478	383	22	63	30.1	35.6	148.8	15
787.5	525	305	26	47	40.9	25.2	120.2	15
918.8	575	221	34	27	68.6	18.3	108.6	15

Ba(OH)₂ Treatment

p.p.m.

Ba(OH) ₂ added as CaCO ₃	Total Resi- due	Alk. to Phen.	Alk. to M.O.	Cal- cium	Magnes- ium	Sul- phates	Chlori- des	Ba.
0	936	0	426	216	55.45	310.9	15	0
668	242	62	162	20.8	4.4	35	15	0
835	137	56	122	14.5	3.6	13	15	0
1002	109	38	66	7.4	0	4	15	0
1169	245	110	148	23.6	0	0	15	90.7
1336	334	200	214	32	0	0	15	181.6

Bloomington



The water supply of the Cunningham Home and the city of Bloomington are obtained from shallow wells and are fairly typical of most waters in central eastern Illinois.

The water supply of Roseville is obtained from shallow wells and is among the hardest of the waters being used in Illinois.

In attempting to obtain quotations on the prices of barium carbonate and barium hydroxide great difficulty was experienced. The following are abstracts of letters received in answer to our inquiries.

"May 27, 1920. Barium carbonate to-day in carloads is worth \$82.50 per net ton, f.o.b. cars our works, Charleston, W.Va., bags extra and returnable. The last price we heard quoted on barium hydroxide was \$125.00 per ton, but we understand the price has materially advanced in the meantime."

"May 29, 1920. Present prices are of course very high, and no one can assume that prices will return to their pre-war values as regards barium products, any more than other products. My understanding is that barium carbonate is now selling at about \$100.00 per ton."

"June 1, 1920. Permit us to inform you that for water purification barium hydrate is not used any more. The reason of this is obvious, because if sulphates are to be precipitated, alkalis or earthly alkalis take their place in the reaction. Therefore, barium carbonate has become the logical water purification material and in times gone by we have sold very large quantities for this purpose. Sulphates are completely precipitated with the generation of CO_2 , which in turn precipitates the iron and leaves the water perfectly pure. Our material is sold as being 98-99% pure barium carbonate, because that is the quality which was shipped

to America before the war, by Germany; but, as a matter of fact, a dry sample of our barium carbonate will assay from 99.2 to 99.6%."

The method of softening water for boiling purposes by the lime-barium treatment has been carried on with considerable success for the past two years⁷ at the Chino Copper Company's plant at Hurley, N.M.

Cost of treatment

Month of February 1919

83 bbl. lime at \$2.18 per bbl.	\$180.94
1040 lbs. BaCO ₃ at \$3.27 per cwt.	34.01
Labor operation	164.00
Miscellaneous supplies	5.84
Steam for injector	<u>5.35</u>
	\$390.14
Cost of treating 1,000 gal. water058

CONCLUSIONS

Barium hydroxide and the lime-barium carbonate methods are satisfactory for the softening of waters having a high sulphate content.

The barium salts yield a water of materially lower total residue upon evaporation and since they do not add to the sodium content of the water have a decided advantage over sodium carbonate in waters which have a tendency to foam.

Because of the insolubility of barium carbonate an excess can be put into the softening apparatus without danger of over treatment.

The time and agitation necessary for complete reaction when using barium carbonate should be further investigated.

While the cost of the barium treatment is greater than the lime-soda ash method the improved quality of the treated water offsets the additional cost. It is possible that the precipitated barium sulphate could be recovered thereby lowering the cost of treatment.

An excess of barium hydroxide should be avoided as it remains in the treated water.

When using the lime-barium carbonate method the excess of barium is too small to be determined by the methods used. Properly controlled treatment with barium hydroxide gives water equally free from barium. Certainly the barium present in the treated water is too small to interfere with any industrial practice and it is highly improbable that it would be injurious for drinking purposes.

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